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Bioaccumulation of Essential and Potentially Toxic Elements in the Muscle and Liver of the Spotted Ratfish (*Hydrolagus colliei*) From Deep-Sea Waters off the Northern Gulf of California

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Abstract

This study aimed to establish the distribution of As, Cd, Cu, Pb, and Zn, in the muscle and liver of the spotted ratfish *Hydrolagus colliei* from the northern Gulf of California to establish the bioaccumulation background data in this species. The individuals ($n = 110$) were obtained by bycatch from the Gulf of California hake fisheries, and the metals and metalloid were measured by atomic absorption spectrometry. The element with the highest concentration in the muscle (15.19 ± 5.40 mg kg^{-1}) and the liver (20.98 ± 10.30 mg kg^{-1}) was As, followed by essential elements (Zn > Cu), and the lowest were the non-essential Pb (0.029 ± 0.014 and 0.048 ± 0.038 mg kg^{-1}, muscle and liver, respectively) and Cd (0.022 ± 0.014 and 0.796 ± 0.495 mg kg^{-1}, muscle and liver, respectively). The liver showed higher bioaccumulation than the muscle in all the studied elements. The sex was not a factor that influenced the bioaccumulation. The concentrations of As in the muscle did not exceed the maximum permissible limits of Mexican legislation, and < 50% of the samples exceed Cd and Pb limits of the Mexican, European Union, and WHO/FAO regulations. The differences found between the elements and tissues could be related to the different diets of the species, their migratory patterns, and their life conditions. Studies in the deep-sea water *H. colliei* are limited, and further investigations are needed regarding the feeding habits of *H. colliei* as well as the interactions of potentially toxic elements within the deep-sea water habitat.

Keywords Chimaera · Chondrichthyan · Trace metals · Pollution

Introduction

The Gulf of California (GC) is of great importance ecological and for fisheries in Mexico, harboring more than 700 fish species, including chondrichthyans or cartilaginous fish. Taxonomically, chondrichthyans are divided in two groups: the Elasmobranchii, including sharks and rays, and the Holocephali including chimeras [1]. Chondrichthyans have been targets of artisanal fishery, with 84.2% of fishing sites on the GC intended for elasmobranch fishing, mainly demersal sharks and rays [2]. Chimeras, such as *Hydrolagus colliei*, are caught in the Pacific hake and deep-sea shrimp fisheries.

The spotted ratfish chimaera (*Hydrolagus colliei*) is distributed from southeastern Alaska to Baja California with depths up to 913 m (British Columbia, Canada); however, studies about its biology had been focused on the coast of Canada and Washington, USA [3, 4], with no available information about the population living in the GC. There is no directed fishery for this species; nevertheless, the tissue is edible and soft, and the liver has been used as a source of oil production [4]. The diet of *H. colliei* consists mainly of mollusks, crustaceans, small fish, echinoderms, and marine worms; it is an important biological resource, and its status in the IUCN (International Union for Conservation of Nature) Red List is of least concern due to an increasing current population trend [5].

Among chemical contaminants, heavy metals, including Cu, Zn, Pb, and Hg, and metalloids, like Se and As, have a great priority because of their high availability, persistence, toxicity, and the potential to bioaccumulate across food chains [6]. These elements can enter aquatic organisms directly through the abiotic environment or the diet; the concentration in the organism can oscillate depending on

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the accumulation and elimination rate [7]. Some organs or tissues are the primary targets for the accumulation of different elements, and in several fish species, most of the metals, metalloids, and other contaminants could accumulate in the liver in comparison with any other tissues [8, 9].

These elements include metals and metalloids which are essential (Cu and Zn) and non-essential or potentially toxic (Cd, Pb, and As) for organisms, and they are distributed and readily bioavailable in aquatic environments. Both essential and non-essential elements can become toxic in lower concentrations; in fact, they are classified as top priority concern in waters by the Agency for Toxic Substances and Disease Registry (ATSDR) where the As, Pb, and Cd are in the top 10 (1, 2, and 7) of list [10]. Copper and Zn are required for certain biochemical reactions in organisms, though, in excess, they can contribute to stress and cause diverse damages in aquatic biota. Cadmium and Pb are known by their partial and total biomagnification in aquatic ecosystems [9], while As is one of the main hazardous substances released in the aquatic environment because of both geogenic and anthropogenic processes [11].

The industrial and artisanal fisheries happening in the GC and the potential harmful effects of these elements for organisms and their consumers make necessary to understand the bioavailability and dynamics of them and the habitat of the species. It should be noted that studies about *H. colliei* are limited, focusing on their biology on the coast of Washington and Canada [3, 4], and for metals, only two studies were found regarding mercury and selenium [12, 13]. This study aimed to measure the distribution of the elements Cu, Zn, Cd, Pb, and As in the muscle and liver of the spotted ratfish *H. colliei* from the northern GC to establish the bioavailable background data in this organism. The hypothesis of this work was to find higher concentrations of essential metals (Cu and Zn) in muscle and liver, than non-essential elements (Cd, Pb, and As) because they are necessary for different metabolic processes; and the liver with higher levels than the muscle due to its regulatory role in the organisms. Also, the muscle (potentially edible) concentrations obtained in this study were compared with the regulations set by the World Health Organization, European Union, and Mexico.

Material and Methods

Sampling and Samples Treatments

The samples were obtained by incidental capture from the Pacific hake fishery, performed in front of San Luis Gonzaga in the northern part of the GC at depths of 110–335 m [14]. The organisms were obtained through the on-board technical program that takes place from January to April each year [14, 15]. A total of 110 *H. colliei* organisms were captured during the years 2015, 2016, and 2017. The measurements of total length (TL) and weight (TW) were obtained, and the sex of the organisms was identified by the absence or presence of the copulatory organ. The liver and muscle were identified, dissected, washed with purified Milli-Q water, and frozen to being freeze-dried for 72 h at −43 °C and 200×10^{-3} mBar. The average moisture percentages were calculated by wet and dry weight differences. The lyophilized (dry) tissues were ground in an agate mortar. Acid digestions were performed on 0.250 g of the homogenized tissues; 5 mL of nitric acid (HNO_3, concentration > 63%, grade trace metals) was added for the muscle and for the liver 3 mL of HNO_3 and 2 mL of hydrogen peroxide (H_2O_2, concentration > 30%). The digestions were carried out by duplicate using Teflon vials in a hot plate at 120 °C for 3 h; once the process was finished, the digested samples were taken to a final volume of 20 mL with Milli-Q water in polyethylene recipients.

Analytic Procedure

Element concentrations were determined by atomic absorption spectrometry (AAS). Copper in the liver and Zn were performed by AAS flame method, while Cu and Cd in the muscle by graphite furnace AAS (Varian, SpectrAA 220). Elemental As and Pb were determined by AAS coupled to a graphite furnace with a Zeeman effect correction system (Analyst 800, PerkinElemer); to achieve optimal analytical performance, matrix modifiers were used for As and Pb. The instrumental conditions are shown in supplementary information (Online Resource 1). The validation of the accuracy, precision, and reliability of the methodology (Table 1) was achieved using the standard reference material DORM-4 (fish protein), certified by the National Research Council in Canada [16] and one blank per each 12 samples of digested batch.

Statistical Analyses

All the data were statistically tested. The descriptive statistics began with an exploratory analysis of the variables and normality test (Kolmogov-Smirnov and Shapiro–Wilk), in addition to Levene test for homoscedasticity in the R software. Residuals were checked to avoid violation of assumptions, and parametric statistics were used. A two-way analysis of variance (ANOVA) was used to establish potential interactions between morphometric data and sex with the elements in tissues; a Student *t* test was used to found differences between sexes for the tissues by elements and Pearson *P* test for correlations between variables. Statistical analyses

Table 1 Reference, obtained, and recovery (± SD) values of standard reference material DORM-4 ($n = 9$)

Element	Reference (mg kg^{-1})	Obtained (mg kg^{-1})	Recovery (%)	DL (µg L^{-1})	CV (%)
Cu[1,2]	15.9 ± 0.9	14.7 ± 1.2	92.2 ± 7.6	0.015	0.7
Zn[1]	52.2 ± 3.2	55.3 ± 4.5	105.9 ± 8.6	0.013	1.3
Cd[2]	0.306 ± 0.015	0.29 ± 0.03	93.5 ± 11.2	0.054	5.2
Pb[2]	0.416 ± 0.053	0.42 ± 0.03	100.8 ± 7.1	0.370	3.7
As[2]	6.80 ± 0.64	6.50 ± 0.20	95.0 ± 3.5	0.350	1.8

[1]Flame AAS. [2]Graphite furnace AAS. *SD*, standard deviation; *n*, sample number; *DL*, instrument detection limit; *CV*, coefficient of variation.

Table 2 Average (± SD) of total length (cm) and weight (g) of the spotted ratfish (*H. colliei*) collected in a three-year sampling by sex

Sex	*n*	TL	LT range	TW	TW range
Female	61	47.2 ± 3.7[a]	34.0–56.5	517.3 ± 121.0[a]	136.0–756.0
Male	49	41.1 ± 1.9[b]	37.5–46.6	297.0 ± 66.4[b]	212.0–590.0
Total	110	44.5 ± 4.3	34.0–56.5	419.2 ± 148.7	136.0–756.0

Different superscript letters indicate significant differences ($p < 0.05$) between male and female TL and TW; *SD*, standard deviation.

were performed with a degree of significance of $p < 0.05$ [17].

Results and Discussion

Biometry

A total of 110 *H. colliei* organisms were captured in a 3-year sampling season. In the sampling year of 2015 one male was captured and 21 females ($n = 22$); the next year (2016) only 9 females were obtained, but in 2017, a total of 79 specimens were caught; 48 were males and 32 were females. Significant differences were found in the variables of TL and TW of the specimens of the spotted ratfish by sex; the females captured during the sampled years had statistically TL ($t = 10.47$) and TW ($t = 11.18$) higher ($p < 0.05$) than the males (Table 2). Also, a strong correlation was found between TL and weight ($r = 0.89$, $p < 0.05$) and followed a potential pattern ($TL = 0.0005\ TW^{3.5671}$), which evidence the peculiar higher sizes and weights of the females.

The reported sizes of *H. colliei* that have been studied over the years were different among the geographic locations where they have been caught [3, 4]. On the Californian and Washington coast, a minimum size of snout-vent length (SVL) of 4.1 cm has been recorded in females and 4.6 cm SVL in males. The maximum sizes reported in females have been 28.3 cm SVL (63.3 cm TL) and in males of 20.8 cm SVL (49.6 TL) [3]. On the coast of British Columbia, sizes higher than 69 cm for females and 67 cm for the males have been recorded [4]. This could indicate a trend of larger sizes at higher latitudes. These studies have also pointed to L_{50} (size when half of the individuals reached the sexual maturity) estimated at 14.9 cm (SVL) for males and 19 cm (SVL) for females [3]. Therefore, the samples obtained from this study suggest that all were adult individuals that have already reached sexual maturity.

The samples of this study were obtained as bycatch fauna in the first months of each year (January to March), and the size range is restricted by the selectivity of the net, so there might be a possible skewness in their capture and may not represent the population of the north GC; however, all other studies have reported that size could be influenced by depth, time of the season (in cold seasons it appears to be a movement toward shallower waters and in warmer ones to deeper [3]), day or night movements (deeper waters during the day and shallower waters at night [4]) therefore more studies would be needed.

Elements Concentration and Correlations in Tissues

The distribution of the elements in *H. colliei* was variable, depending highly on the element and tissue studied. All the results were expressed as mg kg^{-1} on wet weight (ww) basis (Table 3). For tissues, concentration levels in the liver were higher ($p < 0.05$) compared to the muscle, with the following concentration distribution As > Zn > Cu > Pb = Cd.

The differences between the element's concentrations in the liver and muscle of the organism were based on their biological functions; the liver functions consist of metabolizing the substances that arrive through the blood and perform hepatic and pancreatic functions, capturing, storing, and detoxifying pollutants that reach the body [18]; thus, higher concentrations were expected and found in the liver.

Copper concentrations in the muscle ranged from 0.06 to 0.45 mg kg^{-1} (ww) and in the liver from 1.49 to 11.47 mg kg^{-1} (ww), with significant differences between the muscle and liver ($t = -24.77$, $p < 0.05$). Cu showed a significant correlation in the muscle with the TL ($r = 0.22$, $p < 0.05$; Fig. 1) and the TW ($r = 0.26$, $p < 0.05$). In the liver, there were no significant correlations with the morphometric variables of TL and TW ($p > 0.05$). The levels of Cu showed variations by years; for example, the average in

Table 3 Average levels (mg kg.$^{-1}$ ± SD, ww) of Cu, Zn, Cd, Pb, and As in the muscle and liver of the spotted ratfish *H. colliei* by sex

Tissue	Cu	Zn	Cd	Pb	As
Muscle	0.18 ± 0.07^{a}	5.86 ± 3.05^{a}	0.022 ± 0.014^{a}	0.029 ± 0.014^{a}	15.19 ± 5.40^{a}
Female	0.19 ± 0.07^{1}	7.10 ± 3.53^{1}	0.023 ± 0.015	0.033 ± 0.014^{1}	16.53 ± 5.54^{1}
Male	0.15 ± 0.08^{2}	4.32 ± 1.12^{2}	0.021 ± 0.013	0.025 ± 0.014^{2}	13.56 ± 4.80^{2}
Liver	4.35 ± 1.76^{b}	10.19 ± 3.58^{b}	0.796 ± 0.495^{b}	0.048 ± 0.038^{b}	20.98 ± 10.30^{b}
Female	4.53 ± 1.95	11.06 ± 3.65^{1}	0.690 ± 0.330^{1}	0.046 ± 0.043	20.02 ± 8.35
Male	4.13 ± 1.52	9.18 ± 3.25^{2}	0.920 ± 0.617^{2}	0.050 ± 0.032	22.12 ± 12.19

Different superscript letters indicate significant differences ($p<0.05$) between the muscle and liver of each element; different superscript numbers indicate significant differences ($p<0.05$) between male and female of the measured element by tissue; *SD*, standard deviation; *ww*, wet weight basis.

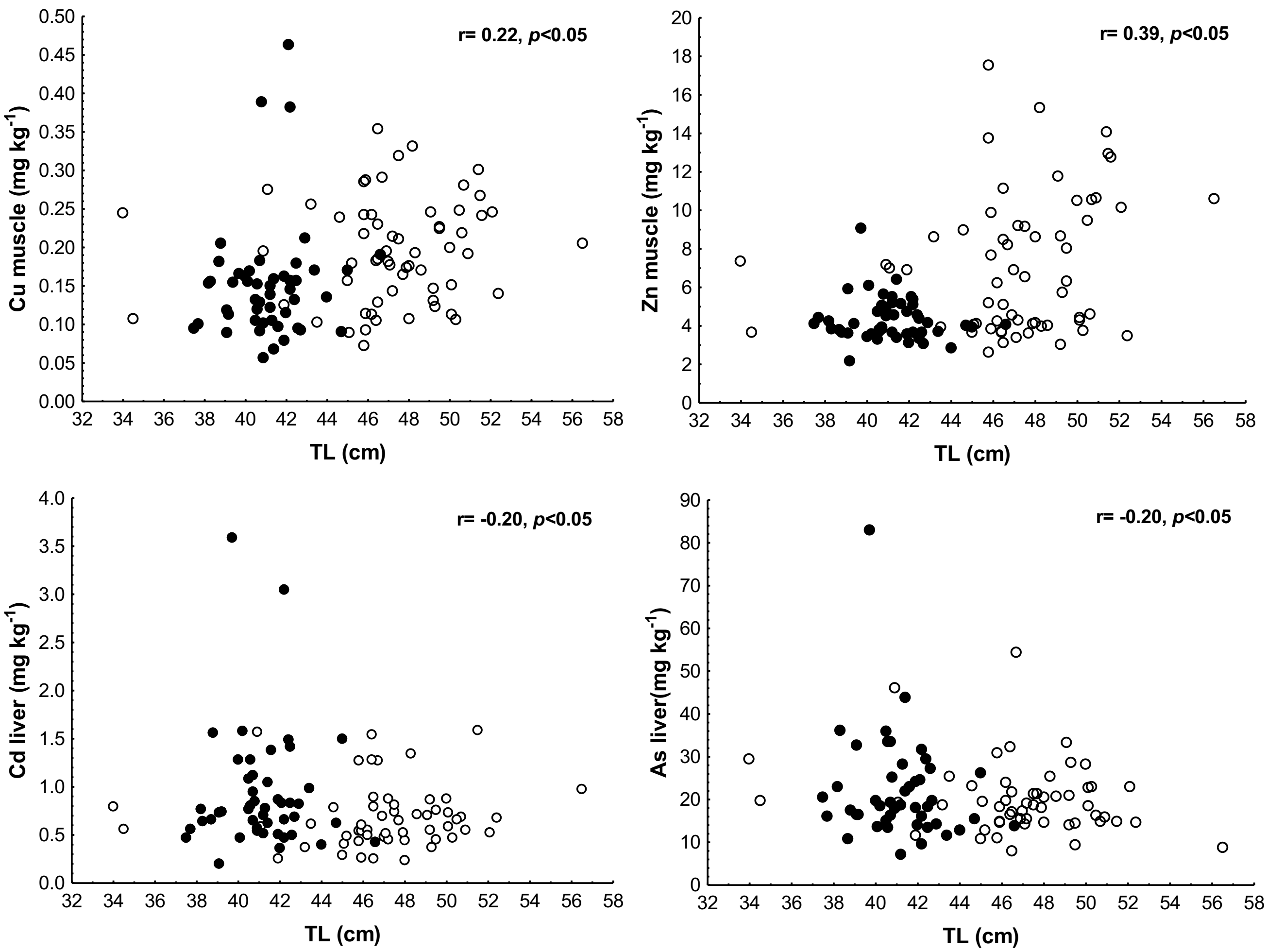

Fig. 1 Correlations between total length (TL) and Cu in the muscle; Zn in the muscle; Cd in the liver; and As in the liver of *H. colliei*. (Black circle) = males and (white circle) = females

2017 (0.15 ± 0.06 mg kg^{-1}) in the muscle was significantly lower ($F=13.10$, $p<0.05$) than the average value from 2015 (0.23 ± 0.06 mg kg^{-1}) and 2016 (0.21 ± 0.04 mg kg^{-1}). Also, the Cu in the liver of 6.40 ± 2.31 mg kg^{-1}, was significantly higher ($F=19.62$, $p<0.05$) in 2015 than 2016 and 2017 (4.41 ± 1.22 and 3.87 ± 1.30 mg kg^{-1}, respectively). The two-way ANOVA showed significant differences between tissues ($F=615.7$, $p<0.05$), but no interaction for sex ($p>0.05$). In general, female had significantly higher ($t=3.11$, $p<0.05$) levels of Cu in the muscle than males (Table 3).

The Zn concentrations in the muscle had a minimum of 2.18 and a maximum of 17.51 mg kg^{-1}; the liver varied in a range of 5.43 up to 28.94 mg kg^{-1}. Zn in the muscle had a significant correlation with the TL ($r=0.39$, $p<0.05$,

Fig. 1) and the TW ($r = 0.39$, $p < 0.05$). In the liver, the TW presented a positive correlation ($r = 0.24$, $p < 0.05$). However, this was not the case for the TL ($p > 0.05$). The average concentrations of Zn in the muscle (10.22 ± 2.66 mg kg^{-1}) and liver (15.58 ± 5.27 mg kg^{-1}) found in the samples from 2015 were significantly higher ($F = 72.16$, $F = 49.34$, respectively, $p < 0.05$) than the other sampling years, followed by 2016 (7.24 ± 2.05 and 11.43 ± 3.22 mg kg^{-1}, in the muscle and liver) and 2017 (4.48 ± 1.78 and 8.84 ± 1.26 mg kg^{-1}, in the muscle and liver). The differences of Zn were evident among tissues ($F = 104.44$, $p < 0.05$) and were significantly influenced by sex ($F = 289.41$, $p > 0.05$). Thus, the Zn in the muscle and liver of the females had significantly higher ($t = 5.30$, $t = 2.74$, $p < 0.05$) levels than the males (Table 3).

Studies on the behavior of elements in marine organisms indicate that Cu is stored mainly in the liver in the form of Cu-protein complexes [19]; this observation agrees with the results of this study, where the Cu in the liver presented significantly higher concentrations (several orders or magnitude, Table 3) than in the muscle. Furthermore, it has been found by radiotracers that most of the incoming Cu taken up by the liver and the muscle ends up with an older Cu fraction [20]. In the case of Zn, it is required in a variety of biological processes, including the metabolism of proteins, nucleic acids, carbohydrates, and lipids, among other functions [21]. However, unlike Cu, Zn does not have a specialized organ for storage; up to 60% of the total Zn in the body is found in the muscle, bone, and skin [21]. Nevertheless, Zn in the muscle was significantly lower than the one found in the liver (Table 3); thus, this might reveal that the liver could be a storage organ for the Zn.

The Cd concentrations in the muscle varied between 0.005 and 0.090 mg kg^{-1} and in the liver between 0.201 and 3.585 mg kg^{-1}, with higher concentrations in the liver ($p < 0.05$). Cd in the liver presented a negative correlation ($p < 0.05$) with TL ($r = -0.20$, Fig. 1). The levels of Cd in the liver were statistically the same ($F = 0.64$, $p = 0.53$) by year; the means were 0.921 ± 0.760, 0.779 ± 0.328, and 0.770 ± 0.437 mg kg^{-1}, for 2015, 2016, and 2017, respectively. Instead, Cd in muscle showed differences among the studied years ($F = 10.98$, $p < 0.05$). The average Cd from 2015 (0.033 ± 0.019 mg kg^{-1}) was statistically higher than that found in 2017 (0.019 ± 0.011 mg kg^{-1}), but was the same as the one from 2016 (0.024 ± 0.009 mg kg^{-1}). The two-way ANOVA showed significant differences between tissues ($F = 270.35$, $p < 0.05$), but not for sex ($p > 0.05$). Contrary to the trends in the essential elements, Cd in the liver of the males was statistically higher ($t = -2.40$, $p < 0.05$) than that found in females.

In the case of Cd, like several non-essential elements, it tends to be easily bioaccumulated in aquatic organisms, entering through the digestive tract or gills and being transferred to multiple tissues, where the liver, kidneys, and gills have relatively higher levels compared to muscle [22]. It has been found that Cd is capable of replacing calcium ions in the body, which allows it to be rapidly absorbed by various organs, especially the liver in short times [23].

Lead concentrations in the muscle presented a minimum of 0.008 to 0.087 mg kg^{-1} and in the liver of 0.010 to 0.271 mg kg^{-1}, with a higher concentration in the liver ($t = -4.74$, $p < 0.05$). The Pb found in the muscle and liver was not statistically correlated to TL nor TW ($p > 0.05$). The Pb in the liver by sampling years 2015, 2016, and 2017 (0.035 ± 0.015, 0.032 ± 0.009, and 0.053 ± 0.042 mg kg^{-1}, respectively) had no differences between each other ($F = 2.33$, $p > 0.05$). But the Pb in the muscle in the year 2017 was statistically lower (0.026 ± 0.013 mg kg^{-1}, $F = 10.77$, $p < 0.05$) than 2016 (0.031 ± 0.014 mg kg^{-1}) and 2015 (0.041 ± 0.014 mg kg^{-1}). The two-way ANOVA showed significant differences between tissues ($F = 32.73$, $p < 0.05$), but not for sex ($p > 0.05$). Again, like Cu and Zn, females had higher levels of Pb in the muscle than the males ($t = 2.73$, $p < 0.05$).

Regarding Pb, the tissues that can bioaccumulate more of this element in fish are the bones, kidneys, liver, gills, and intestines, regardless of Pb concentrations in the environment [24]. Typically, the muscle has lower concentrations than the liver, but for both tissues, Pb was found in lower levels compared to other sensitive tissues such as the bone and kidneys [24]. Pb is capable of inhibiting and replacing Ca ions, and in some cases, also Fe and Zn, although in elasmobranchs, it has been found that it can also affect sodium [24, 25].

The As concentration in the muscle ranged from 4.75 to 37.92 mg kg^{-1} and in the liver from 7.17 to 82.98 mg kg^{-1} with higher concentration in the liver ($t = -5.15$, $p < 0.05$). Arsenic in the liver presented a significant negative correlation with the TL ($r = -0.20$, $p < 0.05$, Fig. 1). The levels of As by years, both in the muscle ($F = 1.45$) and liver ($F = 2.26$), had no variation ($p > 0.05$). For muscle, As means were 15.45 ± 4.71, 17.68 ± 4.91, and 14.84 ± 5.61 mg kg^{-1} and in the liver 25.25 ± 18.36, 23.17 ± 9.75, and 19.74 ± 7.29 mg kg^{-1}, for 2015, 2016, and 2017, respectively, for both tissues. The two-way ANOVA showed significant differences between tissues ($F = 26.94$, $p < 0.05$), but not for sex ($F = 0.230$, $p = 0.63$). In the muscle, females had significantly higher levels of As than males ($t = 2.96$, $p > 0.05$).

Concerning to As, most of this metalloid that has been found in aquatic organisms is in its organic form (arsenobetaine, arsenocholine, and dimethylarsinic acid), while the inorganic species have a minor fraction, although in contaminated areas the proportion can change [26]. Studies of elasmobranchs in the Mediterranean have indicated As concentrations in tissues such as the muscle and liver in different species ranged from 3.27 to 79.27 mg kg^{-1} in the muscle and 0.98 to 26.54 mg kg^{-1} in the liver [27]. The As concentration in the present study was slightly higher than other Mediterranean elasmobranchs; however, much of the concentration of As in fishes is found in organic form, where the inorganic fraction usually has lower proportions, approximately 2% [28]. This may indicate that despite having higher concentrations of As compared to the other elements, it may not cause any problem to the species; it is well known that As found in fish and shellfish is mainly from organic species and is considered non-toxic [26].

Regarding the few significant correlations found among the non-essential elements in the muscle and liver and the variable of total length, this could be related to an increase in levels of these elements in the habitat medium, where bioaccumulation could be higher than the *H. colliei* growth rate [29]. Several activities can contribute to a variety of elements and enrich the waters nearby; the northern GC is a geographical area that exhibits upwelling events and also receives inputs from anthropic activities such as aquaculture and agriculture runoffs, as well as naturals inputs like wind dust from the dessert and hydrothermal vents [9]. Therefore, it was difficult to establish that the study area is polluted since both natural and anthropogenic activities take place.

The annual variability of the elements in relation to the total mean concentration was low; the year 2015 had the higher values for all the elements, but the number of items caught were 22 (1 male and 21 females); 9 females were obtained in 2016 and 79 organisms in 2017 (48 males and 31 females); differences in numbers could influence variability rather than annual conditions. There was also a notorious difference in accumulation patters followed by females and males; females had higher Cu, Zn, Pb, and As in the muscle than males, as well as higher Zn in the liver (Table 3). First, the number or female organisms (61) were higher than males (49); thus, the size segregation and different feeding patterns might be key factors. The organisms of bigger sizes (females in our study) prefer shallow waters, and this represents high variability and availability of potential prey species, leading to different feeding habits [3, 4].

Relationships Among the Studied Tissues and Elements

Among the studied elements in the muscle and liver, several correlations were established ($p < 0.05$). The levels of Cu found in the muscle were correlated to Zn, Cd, Pb, and As, as well in the muscle ($p < 0.05$, Table 4); the Cu in the muscle was also significantly correlated to Cu, Zn, Cd, and Pb in the liver. The concentrations found for Zn in the muscle also established significant correlations between the elements in all the studied tissues ($p < 0.05$) except for Cd and Pb in the liver ($p > 0.05$). The non-essential elements were significant less related to each other than the essentials (Table 4).

Interactions of the essential elements Cu and Zn with the non-essential elements are commonly established but not well understood. For instance, some Cu and Zn proteins can interact with elements like Cd, having a Cu–Zn-Cd relation, but this does not interfere with the Ca competition by Cd [21, 23]. As it is well known, Pb has been found capable of replacing essential elements like Zn [24]; thus, it was expected a negative correlation between Pb and Zn, but the opposite happened in this study. Further studies are needed to fully understand the relationships and interactions between the analyzed elements in each tissue in this deep-water species.

Comparisons with National and International Legislation

There are only two studies with information about levels of Hg in tissues of *H. colliei*, and those authors compared legislation limits established for fish consumption focused on Hg. There are no previous data on the elements studied

Table 4 Pearson correlations ($p < 0.05$) between the elements and the studied tissues of *H. colliei* from the northern Gulf of California

	Cu_{mus}	Zn_{mus}	Cd_{mus}	Pb_{mus}	As_{mus}	Cu_{liv}	Zn_{liv}	Cd_{liv}	Pb_{liv}	As_{liv}
Cu_{mus}	-	0.51	0.37	0.23	0.27	0.33	0.31	0.21	-0.28	NS
Zn_{mus}	0.51	-	0.36	0.39	0.27	0.44	0.59	NS	NS	0.21
Cd_{mus}	0.37	0.36	-	0.25	NS	0.22	0.22	0.30	NS	NS
Pb_{mus}	0.23	0.39	0.25	-	NS	0.21	NS	NS	NS	NS
As_{mus}	0.27	0.27	NS	NS	-	NS	NS	NS	NS	0.23
Cu_{liv}	0.33	0.44	0.22	0.21	NS	-	0.81	0.45	NS	0.47
Zn_{liv}	0.31	0.59	0.22	NS	NS	0.81	-	0.39	NS	0.61
Cd_{liv}	0.21	NS	0.30	NS	NS	0.45	0.39	-	NS	0.60
Pb_{liv}	-0.28	NS	NS	NS	NS	NS	NS	NS	-	NS
As_{liv}	NS	0.21	NS	NS	0.23	0.47	0.61	0.60	NS	-

NS, not significant ($p > 0.05$).

in this work for the species *H. colliei*. and by comparing the results of Cu, Zn, Cd, Pb, and As obtained in the muscle with international regulations, Cd did not exceed the regulations of Mexico (0.5 mg kg^{-1}) [30] and the WHO [31], but 5.5% of the samples exceeded the limit of 0.05 mg kg^{-1} of Cd considered by the European Union [32]. Pb exceeded the Mexican limits (0.5 mg kg^{-1}) in 8.25% of the samples, and 43.11% of the samples exceeded the regulations by the WHO and EU (0.3 mg kg^{-1}). In the case of As, it did not exceed the regulations of Mexico and the USA (80.0 mg kg^{-1}) [30, 33]; however, this is considered for crustaceans and mollusks.

Comparison of Elements in the Tissues of *H. colliei* with Other Chondrichthyans of the Study Area

Currently, the spotted ratfish (*H. colliei*) is not of commercial interest in Mexico, and there are not studies related to Cu, Zn, Cd, Pb, and As and the dynamics in *H. colliei* tissues. However, there are several studies in relation to these metals in chondrichthyans in the GC. The concentration levels of Cu and Zn in these organisms are diverse, having a high range of differences between certain species, and others were similar (Table 5). It is important to highlight that the comparisons were mainly among sharks, because there is only one global study about batoids from the study area. No other chimeras were available to compare these elements (Table 5).

The levels of As, Cd, and Pb found in the pelagic thresher shark, *Alopias pelagicus*, were the highest concentrations found in the muscle of the chondrichthyans of GC [39] and were followed by batoids [40] in comparison to the lower results for the spotted ratfish from this study; other sharks like the Pacific sharpnose shark, *Rhizoprionodon longurio* [34], and the scalloped hammerhead, *Sphyrna lewini* [35], had lower concentrations of Cd than *H. colliei*. Nevertheless, the Pb in the muscle of *R. longurio* was the second highest measured of the chondrichthyans of GC, thus higher than the results for *H. colliei* from this study. The shark *S. lewini* had similar levels of Pb in the liver, but lower Cd than the spotted ratfish (Table 5). Arsenic is a metalloid poorly studied in the organisms of GC, but the levels found in the muscle and liver of *H. colliei* were higher than the other species from the area. The essential element Cu found in other chondrichthyans species from the GC was higher than the results from this work for *H. colliei* in the muscle, but in the liver, Cu was higher than the found in the sharks *R. longurio*, *S. lewini*, and *R. typus* and only exceeded by the batoids from the study area. Instead, Zn levels were variable among species; in the muscle and liver of *H. colliei*, Zn was higher than the found for *R. longurio* and *S. lewini*, but lower than the species *R. typus*, *A. pelagicus*, and the batoids.

The differences between the concentrations of elements of the chondrichthyans that inhabit the GC may be due to the differences in biology (metabolism, life cycle, feeding habits, rates of accumulation-excretion) and life history (exposure and migration) of the species. For example, *R. typus* is a highly migratory species with a global distribution through the tropics, feeding on small plankton and nekton [41]. The shark *S. lewini* has a similar distribution to *R. typus* but with less migration and feeds on cephalopod and teleost fish [42]. While *H. colliei* has an

Table 5 Levels of essential and non-essential elements (mg kg^{-1} ± SD, ww) in chondrichthyans of GC

Species/tissues	Trophic level	Cu	Zn	Cd	Pb	As
Rhizoprionodon longurio[34]	4.2					
Muscle		0.21 ± 0.04	3.04 ± 0.41	0.005 ± 0.005	0.89 ± 1.05	NA
Liver		1.08 ± 0.33	5.61 ± 1.87	0.75 ± 0.53	< DL	NA
Sphyrna lewini[35, 36]	4.1					
Muscle		0.28 ± 0.05	3.05 ± 0.39	0.004 ± 0.002	0.01 ± 0.01	10.10 ± 2.10
Liver		1.76 ± 1.18	8.07 ± 2.86	0.23 ± 0.14	0.04 ± 0.02	9.40 ± 3.00
Batoids [37]	-					
Muscle		0.74 ± 0.43	7.20 ± 2.80	0.06 ± 0.06	0.31 ± 0.24	20.9 ± 19.6
Liver		5.24 ± 5.51	14.4 ± 6.2	0.32 ± 0.23	0.76 ± 0.38	7.40 ± 3.50
Rhincodon typus [38]	3.6					
Muscle		0.92	8.49	NA	NA	NA
Liver		1.59	9.52	NA	NA	NA
Alopias pelagicus [39, 40]	4.5					
Muscle		24.7 ± 18.3	189.4	1.3 ± 1.5	2.6 ± 2.6	43.2
Liver		NA	NA	86.5 ± 56.4	NA	NA
*H. colliei**	3.7					
Muscle		0.18 ± 0.07	5.86 ± 3.05	0.022 ± 0.014	0.029 ± 0.014	15.19 ± 5.40
Liver		4.35 ± 1.76	10.19 ± 3.58	0.796 ± 0.495	0.048 ± 0.038	20.98 ± 10.30

*This study; *SD*, standard deviation; *ww*, wet weight.

apparently isolated population in the north of the GC, it is distributed along the eastern coast of the Pacific Ocean, feeding on mollusks, crustaceans, and fish [5]. Therefore, it can be considered that this deep-water species has an advantage because it could reflect the environmental conditions for these elements in the waters of the northern Gulf of California and its potential toxic effects.

Conclusion

The distributions of elements in the spotted ratfish depended strongly on the type of tissue. In all the elements, the liver presented higher concentrations than in the muscle. The sex was not an important influencing factor for metal bioaccumulation, although the female had higher total lengths and weights. Arsenic was the element with the highest concentrations followed by the essentials and finally the non-essential (As > Zn > Cu > Pb–Cd); thus, these results partially confirm the proposed hypotheses. The concentration of As did not exceed the maximum permissible limits of Mexican regulations, but 5.5% of the samples exceeded the Cd limits by the EU, while Pb exceeded the limits of Mexican regulations in 8.2% and in 43.1% of the WHO and the EU. The differences found in the studied elements in *H. colliei* and other chondrichthyans from GC could be related to the different diets of the species, their migratory patterns, and their life conditions. Further investigations are needed regarding the feeding habits of *H. colliei* as well as the interactions within the deep-water habitat, to have a better understanding of their diet and their role in the ecosystem as well in the food chain.

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Author Contribution All authors contributed to the study conception and design. Material preparation, data collection, methodology, and investigation were performed by Magdalena E Bergés-Tiznado and Víctor Manuel Tiznado-Salazar. Statistical analyses were performed by Víctor Manuel Tiznado-Salazar and Oscar G. García-Zamora. Conceptualization and validation were performed by Carolina Bojórquez-Sánchez, J. Fernando Márquez-Farías, Oscar G. Zamora-García, and Federico Páez-Osuna. The first draft of the manuscript was written by Víctor Manuel Tiznado-Salazar, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data Availability The datasets generated during and/or analyzed during the current study are not publicly available but are available from the corresponding author on request.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent to Publish Not applicable.

Competing Interests The authors declare no competing interests.

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